

Sorption-Enhanced Reaction Process for Hydrogen Production

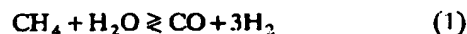
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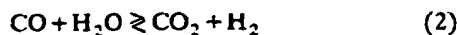
A novel concept called Sorption Enhanced Reaction Process (SERP) for hydrogen production by steam-methane reformation (SMR) reaction uses a fixed packed column of an admixture of an SMR catalyst and a chemisorbent to remove carbon dioxide selectively from the reaction zone. The chemisorbent is periodically regenerated by using the principles of pressure swing adsorption. The SERP process steps allow direct production of high-purity hydrogen (> 95 mol %) at high methane to hydrogen conversion (> 80%) with dilute methane (< 5 mol %) and trace carbon oxide (~ 50 ppm) impurities at the reaction pressure by operating the reactor at a low temperature of 450°C. A conventional plug-flow reactor packed with catalyst alone not only needs to be operated at a much higher temperature (> 650°C) to achieve the same methane to hydrogen conversion, but produces a much lower purity of hydrogen product (~ 75 mol %) with a large quantity of carbon oxide (~ 20 mol %) impurities. A novel chemisorbent, which reversibly sorbs carbon dioxide in the presence of excess steam at a temperature of 300–500°C, was developed for application in the SERP and the process is experimentally demonstrated in a bench-scale apparatus.

Introduction

The most common industrial process for production of hydrogen uses the endothermic steam-methane reformation (SMR) reaction (Leiby, 1994)



It is generally carried out in a catalytic (Ni on alumina) reactor at a pressure of 50–600 psig and a temperature of 750–900°C. The reactor feed gas is a mixture of steam and methane (natural gas) in the ratio of 2.5–6.0. The reactor effluent gas typically contains 70–72% H₂, 6–8% CH₄, 8–10% CO, and 10–14% CO₂ on a dry basis. This gas is cooled in a waste heat boiler (steam produced) and fed to another catalytic (Fe or Cu on alumina) reactor for the exothermic water-gas shift (WGS) reaction (Leiby, 1994)



The high temperature WGS reactor is generally operated at a temperature of 300°–400°C. The effluent gas from the reactor typically contains 71–75% H₂, 4–7% CH₄, 1–4% CO and 15–20% CO₂ on a dry basis. The effluent is further cooled to a temperature of 20°–50°C (more steam is produced and water is condensed) and fed to a multicolumn pressure swing adsorption (PSA) process at a pressure of 50–600 psig. The PSA feed gas is saturated with water. The PSA process produces a hydrogen product stream containing dry 98–99.999+% H₂ at the feed gas pressure with a H₂ recovery of 70–90%. The waste gas from the PSA process containing unrecovered H₂ and all of feed H₂O, CH₄, CO and CO₂ is produced at a pressure of 2–10 psig, and it is used as part of the fuel required to supply the heat of the endothermic SMR reaction. Natural gas provides the balance of the required fuel. Figure 1 shows a block diagram for the above described SMR-WGS-PSA process train for production of pure H₂ (Leiby, 1994).

A multicolumn PSA process containing 4–12 adsorption beds is generally used (Wagner, 1969; Fuderer and Rudelstorfer, 1976; Sircar and Kratz, 1988) in conjunction with a

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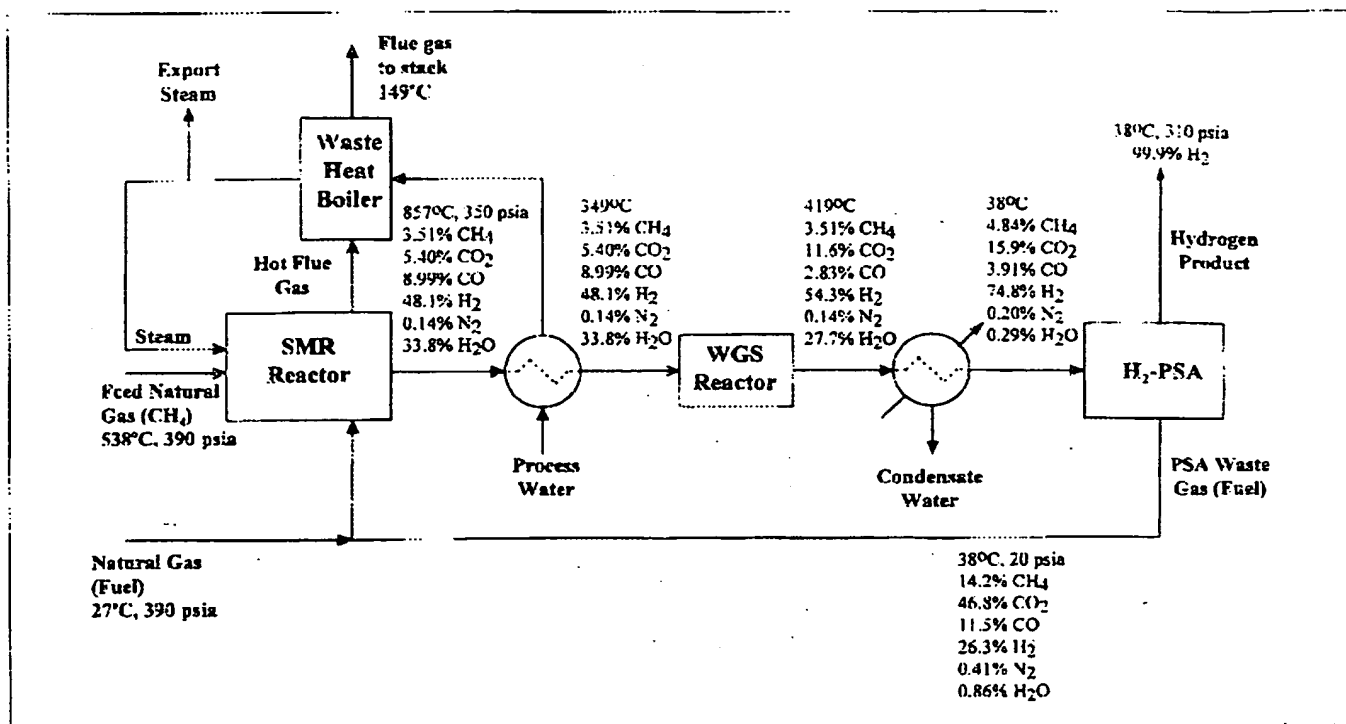


Figure 1. Conventional SMR process for hydrogen production.

combination of various PSA process steps (adsorption, cocurrent depressurization, countercurrent depressurization and purge, vacuum purge, cocurrent and countercurrent pressure equalization, feed and product pressurization, and so on). The net H₂ recovery from the PSA process and its adsorbent inventory depend on many variables like feed gas pressure and composition; design; operating conditions and cycle times of the PSA process steps; H₂ product purity; and so on. In particular, the CO and CO₂ concentrations of the feed gas are critical in determining the design and efficiency of separation of the PSA process because bulk CO₂ is difficult to desorb and dilute CO is difficult to adsorb.

The heat of reaction is supplied to the SMR reactor by combusting fresh natural gas and H₂-PSA waste gas. The radiant thermal efficiency of the SMR reactor is typically 40–50%. The overall thermal efficiency of the SMR H₂ production unit, on the other hand, is about 85%. This is achieved by recovering waste heat from the reformer flue gas at the cost of additional heat-transfer equipment. The excess heat is partly recovered in the form of steam and the excess steam (over what is needed for SMR reaction) is often exported from the hydrogen production site.

The high-temperature operation of the SMR reactor, the catalyst deactivation due to coking, the use of high-temperature metallurgy for construction of the SMR reactor, the requirement of large interstage heat recovery systems, and the complex design of the multicolumn H₂-PSA system significantly raises the capital cost of H₂ production. Nevertheless, the SMR-WGS-PSA process, described by Figure 1 remains the most cost-effective method for production of pure H₂ in the commercial scale (1–100 MM SCFD H₂). The technology

has been improved during the last 60 years through numerous innovations in the areas of natural gas desulfurization, SMR and WGS catalysis, reactor design, heat supply and removal systems, PSA process design and adsorbents, process control, heat generation and management, and so on. It will be extremely desirable if newer concepts for production of H₂ by SMR can be developed which reduce the capital cost compared to the conventional route.

In previous publications (Sircar et al., 1995; Carvill et al., 1996), we described a concept called Sorption Enhanced Reaction Process (SERP) which can yield high conversion of reactants to products for an equilibrium-controlled, endothermic reaction at a much lower temperature than would be necessary by a conventional catalytic reactor due to thermodynamic limits. The concept is based on Le Chatelier's principle that (a) the conversion of reactants to products and (b) the rate of forward reaction in an equilibrium controlled reaction can be increased by selectively removing some of the reaction products from the reaction zone. The SERP uses a selective adsorbent (admixture with the catalyst in the reactor) for selective removal of a reaction product and the adsorbent is periodically regenerated (adsorbed component is desorbed) by using the principles of PSA. A specific design of the PSA cycle and a specific method of its operation makes the SERP concept very efficient by (a) directly producing the desired reaction product at high purity and conversion at reaction pressure, (b) permitting the operation of the reactor at a much lower temperature (cheaper metallurgy and heat exchange equipment), and (c) drastically reducing or eliminating the subsequent product purification requirements (cheaper product purification). The concept was demon-

strated experimentally for the production of pure CO by reacting CO₂ and H₂ (reverse water gas shift reaction according to Eq. 2) using a commercial WGS catalyst and NaX zeolite as the adsorbent for selective removal of a reaction product (H₂O) from the reaction zone (Carvill et al., 1996). The purpose of this article is to demonstrate the applicability of SERP concept for the production of H₂ by SMR.

Steam Methane Reforming

Both SMR and WGS reactions take place in the SMR reactor. The thermodynamic equilibrium constants (K) for these reactions, which are functions of reaction temperature only, may be written as

$$K_{\text{SMR}}(T) = \frac{P^2(y_{\text{H}_2})^3(y_{\text{CO}})}{(y_{\text{CH}_4})(y_{\text{H}_2\text{O}})} \quad (3)$$

$$K_{\text{WGS}}(T) = \frac{(y_{\text{CO}_2})(y_{\text{H}_2})}{(y_{\text{CO}})(y_{\text{H}_2\text{O}})} \quad (4)$$

Equations 3 and 4 describe the equilibrium relationships between gas-phase mole fractions of component i (CH₄, CO, CO₂, H₂O and H₂) in a batch reactor at a total gas phase pressure P and temperature T . They can be rearranged to obtain

$$y_{\text{H}_2} = \frac{[K_{\text{SMR}}K_{\text{WGS}}]^{0.25}}{[P]^{0.5}} \cdot \frac{[y_{\text{CH}_4}]^{0.25} [y_{\text{H}_2\text{O}}]^{0.5}}{[y_{\text{CO}_2}]^{0.25}} \quad (5)$$

$$y_{\text{CO}} = \frac{[K_{\text{SMR}}]^{0.25}}{[K_{\text{WGS}}]^{0.75} [P]^{0.5}} \cdot \frac{[y_{\text{CH}_4}]^{0.25} [y_{\text{CO}_2}]^{0.75}}{[y_{\text{H}_2}]^{0.5}} \quad (6)$$

Equation 5 shows that the gas-phase H₂ mole fraction can be increased by decreasing the corresponding CO₂ mole fraction. Equation 6 shows that the gas-phase CO mole fraction decreases as the corresponding CO₂ mole fraction decreases. More importantly, these equations show that a very high conversion of CH₄ to H₂ can be achieved in a SMR reactor even at a moderate temperature (low K_{SMR}) if CO₂ is removed from the reaction zone. At the same time, the co-production of CO will be suppressed.

Figure 2 shows plots of K_{SMR} and K_{WGS} as functions of T (Twigg, 1989). The equilibrium constants increase and decrease exponentially with increasing T for the SMR and WGS reactions, respectively. The figure also shows the batch conversion of CH₄ to H₂ as a function of T for a feed mixture containing a H₂O/CH₄ ratio of 6:1 at a constant reactor pressure of 50 psig. The conversion decreases drastically as the reaction temperature falls below 650°C. These conversion numbers were calculated by simultaneously solving Eqs. 3 and 4 with the appropriate mass balance equations for a constant pressure and a constant temperature batch reactor system.

We now examine a constant temperature (T) and constant pressure (P) batch SMR reactor where the CO₂ produced by reactions 1 and 2 is selectively removed from the gas phase by adsorption. It can be shown that the equilibrium gas-phase

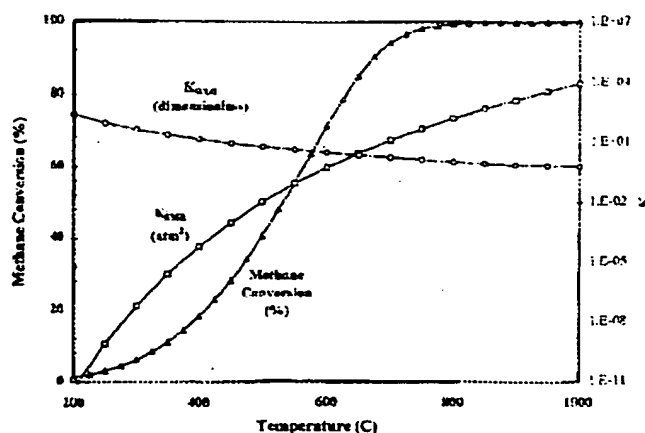


Figure 2. Temperature dependence of equilibrium constants for SMR and WGS reactions, and batch conversions of CH₄ to H₂ for a 6:1 H₂O/CH₄ reactor feed at 50 psig (445.8 kPa).

mole fractions in such a system are given by

$$y_{\text{H}_2} = \frac{(3\beta + \delta)}{(1 + 2\beta - f\delta)}; \quad y_{\text{CH}_4} = \frac{1 - \beta(1 + \alpha)}{(1 + \alpha)(1 + 2\beta - f\delta)};$$

$$y_{\text{H}_2\text{O}} = \frac{\alpha - (\beta + \delta)(1 + \alpha)}{(1 + \alpha)(1 + 2\beta - f\delta)}; \quad y_{\text{CO}} = \frac{(\beta - \delta)}{(1 + 2\beta - f\delta)};$$

$$y_{\text{CO}_2} = \frac{(1 - f)\delta}{(1 + 2\beta - f\delta)} \quad (7)$$

where α is the molar ratio of feed H₂O/CH₄ introduced into the batch reactor at P and T , β is the moles of CO produced by the SMR reaction per mole of the feed gas, δ is the moles of CO reacted by the WGS reaction per mole of the feed gas, and f is the fraction of CO₂ produced by the WGS reaction that is removed from the gas phase by adsorption. The variables α , β , and δ are related by the thermodynamic equations.

$$K_{\text{SMR}}(T)$$

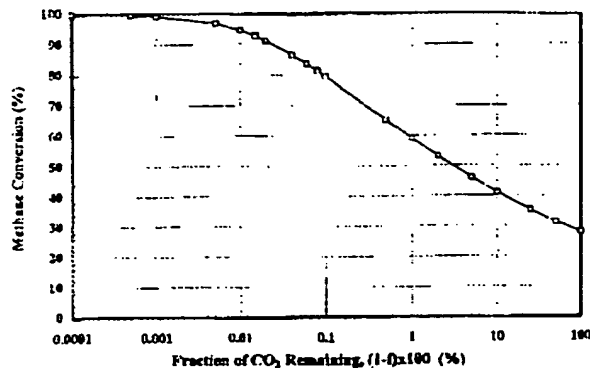
$$= \frac{P^2(\beta - \delta)(3\beta + \delta)^3(1 + \alpha)^2}{[1 + 2\beta - f\delta]^2[1 - \beta(1 + \alpha)][\alpha - (1 + \alpha)(\beta + \delta)]} \quad (8)$$

$$K_{\text{WGS}}(T) = \frac{(1 - f)\delta(3\beta + \delta)(1 + \alpha)}{(\beta - \delta)[\alpha - (\beta + \delta)(1 + \alpha)]} \quad (9)$$

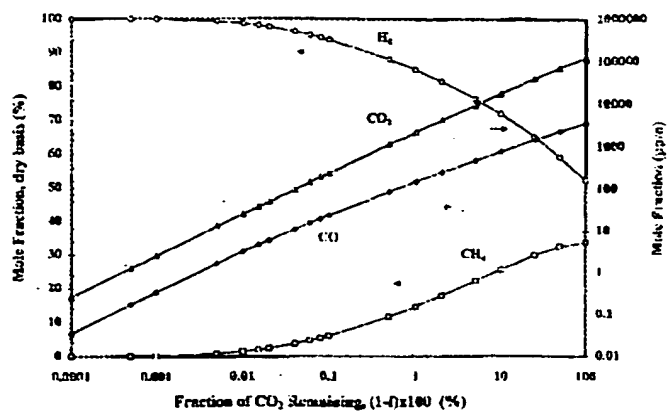
The moles of H₂ formed per mole of CH₄ introduced into the reactor (χ) is given by

$$\chi = (3\beta + \delta)(1 + \alpha) \quad (10)$$

Equations 8 and 9 can be simultaneously solved for a given set of values of P , T and α in order to calculate β and δ as



(a)



(b)

Figure 3. Performance of batch SMR reactor for a 6:1 $\text{H}_2\text{O}/\text{CH}_4$ reactor feed at 450°C and 50 psig (445.8 kPa).

(a) Equilibrium conversion of CH_4 to H_2 with CO_2 removal from reaction zone; (b) equilibrium gas phase composition with CO_2 removal from reaction zone.

functions of f . Then, Eqs. 7 and 10 can be used to calculate equilibrium gas-phase mole fractions of all components and the CH_4 to H_2 conversion ($=\chi/4$) in the batch reactor as functions of f .

Figures 3a and 3b show the results of above described calculations for $\alpha = 6:1$, $P = 50$ psig, and $T = 450^\circ\text{C}$. Figure 3a plots the conversion of CH_4 to H_2 as a function of $\ln(1-f)$, and Figure 3b shows the corresponding dependence of gas-phase mole fractions (dry basis) as functions of $\ln(1-f)$. The conversion numbers depicted by Figure 2 can be obtained by setting $f = 0$ in Eqs. 7–10. Figures 3a and 3b clearly demonstrate that (a) very high conversion of CH_4 to H_2 ($> 80\%$) by the SMR-WGS reactions can be achieved at a moderate temperature of 450°C , and (b) a gas phase, which has a large H_2 mole fraction ($> 95\%$) and which is essentially free of carbon oxides (< 100 ppm) on a dry basis, can be produced when 99.9% or more of the CO_2 produced by the reactions is removed by the adsorbent. The corresponding CH_4 to H_2 conversion for the case where CO_2 is not removed from the reaction zone is only 28.0% (Figure 2) and the equilibrium gas-phase mole fractions are 52.8% H_2 , 33.8% CH_4 , 12.9% CO_2 , and 0.34% CO (dry basis). Thus, all the key advantages of the SERP concept described earlier can be realized for production of H_2 by reacting H_2O and CH_4 in a reactor packed with an admixture of SMR catalyst and a CO_2 selective adsorbent.

CO_2 Adsorbent for H_2 -SERP

A key requirement for practical utilization of the SERP concept for H_2 production by SMR is the availability of an adsorbent which can selectively remove CO_2 from the SMR reaction zone at moderately high temperatures ($300^\circ\text{--}500^\circ\text{C}$) in the presence of a large partial pressure of steam. The other requirements are that (a) the adsorbent can be regenerated using the principles of PSA, (b) the adsorbent exhibits a substantial CO_2 working capacity between the conditions of the adsorption and desorption steps of SERP, (c) the kinetics of ad(de)sorption of CO_2 is relatively fast, and (d) the material

is stable in presence of steam and has adequate mechanical strength.

To our best knowledge, there is no commercially produced adsorbent that satisfies the above requirements. So, we developed a proprietary material which reversibly chemisorbs CO_2 in the temperature range of $300\text{--}500^\circ\text{C}$ in the presence of excess steam (Anand et al., 1996; Hufton et al., 1998). The material is a potassium carbonate promoted hydrotalcite (pelletized form).

The reversible CO_2 ad(de)sorption property of the proprietary chemisorbent is demonstrated by Figure 4. It plots the net CO_2 working capacity at a temperature of 400°C . The data are generated by exposing the chemisorbent to a dry gas mixture containing CO_2 (70%) and N_2 (30%) at a total gas pressure of one atmosphere (adsorption) for a period of one

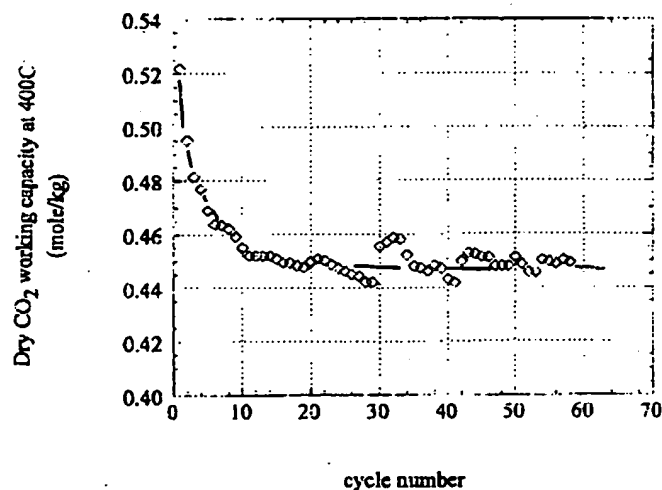


Figure 4. Dry CO_2 working capacity on chemisorbent cycled between CO_2 partial pressures of 0.7 and 0.0 atm at 400°C as functions of cycle number.

hour in a conventional micro balance followed by exposing the material to pure and dry N_2 at a pressure of one atmosphere (desorption) for one hour (Anand et al., 1996). The difference in the weights of the material under these two conditions is defined as the net CO_2 working capacity. This ad(desorption) process was repeated over many cycles. Figure 4 plots the net CO_2 working capacity as a function of the cycle numbers. It shows that a stable reversible CO_2 working capacity of ~ 0.45 mol/kg is achieved by the material after 10 cycles of operation. The CO_2 working capacity decreases during the first 10 cycles indicating that a certain portion of CO_2 is irreversibly chemisorbed on the material.

The net CO_2 working capacity of the material in the presence of steam was measured by flowing a gaseous mixture of CO_2 and H_2O (CO_2 partial pressure of 0.3 atm and steam partial pressure of 10 atm) at $400^\circ C$ over the chemisorbent contained in a small thermostated chamber until the effluent gas CO_2 concentration was equal to that of the feed gas. The chemisorbed CO_2 was then desorbed by flowing dry CO_2 -free N_2 over the sample at $400^\circ C$ and ambient pressure while monitoring the effluent gas-flow rate and its CO_2 concentration. The net working CO_2 capacity was estimated by the amount of CO_2 desorbed. This ad(desorption) experiment was also carried out over many cycles. Figure 5 shows the results. It may be seen that the CO_2 working capacity for chemisorption on the material at $400^\circ C$ in the presence of steam became practically constant after 10 cycles of exposure to CO_2 -steam mixture indicating reversible chemisorption. Again, the CO_2 working capacity decreased during the initial ad(desorption) cycles due to some irreversible chemisorption. A comparison of the data in Figures 4 and 5 shows that the net reversible CO_2 working capacity on the chemisorbent at $400^\circ C$ is not affected by the presence of excess steam in the gas phase. The crush strengths of the pelletized chemisorbent were very similar before and after exposure to steam (Hufon et al., 1998).

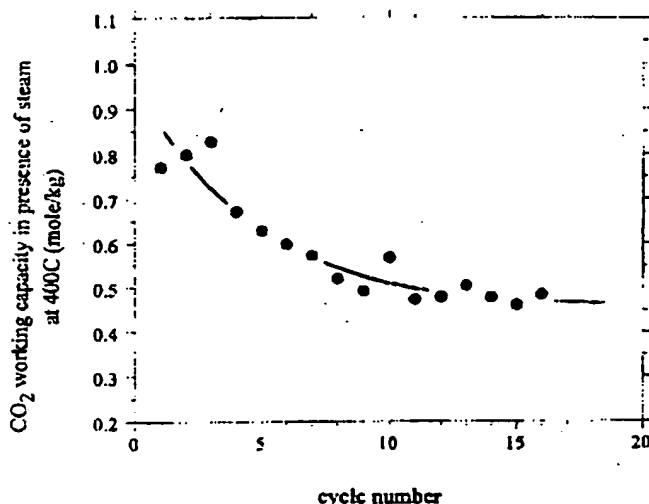


Figure 5. CO_2 working capacity on chemisorbent cycled between CO_2 partial pressures of 0.3 and 0.0 atm in presence of steam (partial pressure ~ 10 atm) at $400^\circ C$ as functions of cycle number.

Sorption Properties of the Chemisorbent

We measured the equilibrium isotherm, the kinetics, and the desorption characteristics for sorption of dry CO_2 on the chemisorbent at $400^\circ C$ using a column apparatus. It consisted of a stainless steel column (internal diameter = 1.1 cm; length = 205.7 cm) packed with 160 g of the chemisorbent (0.16-cm-diameter pellets). It was thermostated at $400^\circ C$ using electric heaters. The column was initially filled with pure N_2 at atmospheric pressure and $400^\circ C$. Preheated $CO_2 + N_2$ mixtures containing different mole fractions of CO_2 were then passed through the column at constant flow rates (Q°) at near ambient pressures. The effluent gas-flow rate [$Q(t)$] and CO_2 concentration [$y(t)$] were monitored as functions of time (t) until complete breakthrough of CO_2 (effluent gas concentration is the same as that of feed) occurred. The CO_2 was then desorbed by flowing pure N_2 through the column at a constant flow rate (Q°) at near ambient pressure. The effluent gas-flow rate [$Q(t)$] and its CO_2 concentration [$y(t)$] were again monitored as functions of time (t). A continuous infrared CO_2 (Beckman) analyzer was used for measurement of CO_2 concentrations. The void volume in the column was measured by the conventional helium expansion technique. The experiments were conducted after repeatedly exposing the material to CO_2 at $400^\circ C$ and then regenerating it by N_2 purge in order to saturate the column with irreversibly adsorbed CO_2 .

The adsorption capacity of the chemisorbent at different partial pressures of CO_2 ($0 \leq p_{CO_2} \leq 1$) at $400^\circ C$ were estimated by carrying out material balances in conjunction with the adsorption breakthrough data (Sircar and Kumar, 1983). Figure 6 shows an example of the reversible CO_2 chemisorption isotherm on the material at $400^\circ C$. It plots the fractional coverage of CO_2 (θ) as a function of equilibrium gas-phase CO_2 partial pressure (p_{CO_2}). The fractional coverage is defined by the ratio of actual amount of CO_2 adsorbed to the saturation CO_2 capacity. These data were measured using one batch of the material. The saturation capacity somewhat varied from batch to batch.

It may be seen from Figure 6 that the CO_2 isotherm is rather steep in the low CO_2 partial pressure region. The

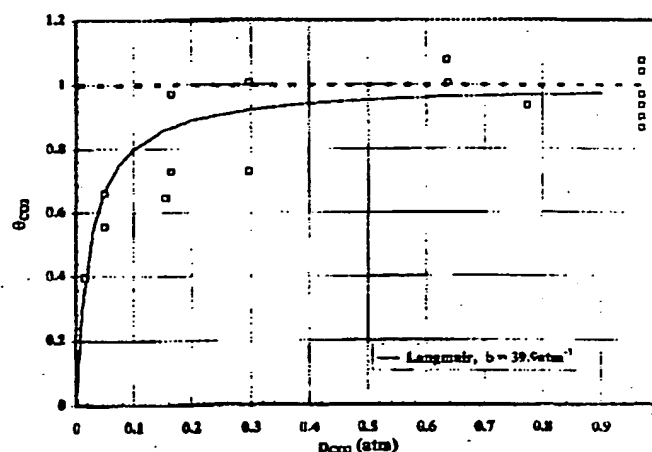


Figure 6. Reversible sorption isotherm of CO_2 on chemisorbent at $400^\circ C$.

fractional coverage of CO_2 approaches unity when $p_{\text{CO}_2} \geq 0.3$. This explains the similarity between the net CO_2 working capacities of Figures 4 and 5 which were measured using p_{CO_2} values of 0.7 and 0.3, respectively. The chemisorption isotherm of Figure 6 is Type I in shape by Brunauer classification (Young and Crowell, 1962; Hayward and Trapnell, 1964), and it can be described by the Langmuir model $\{\theta = bp_{\text{CO}_2}/(1 + bp_{\text{CO}_2})\}$ where b is the Langmuir gas-solid interaction parameter. The solid line of Figure 6 gives the best fit of the data [$b = 39.9 \text{ atm}^{-1}$] by the model.

Figure 7 shows an example of CO_2 adsorption breakthrough data on the material at 400°C . It was generated by using a CO_2 feed gas mole fraction of 0.657 (y^0) at a feed mass-flow rate of $3.0 \times 10^{-5} \text{ gmol/cm}^2/\text{s}$ (based on empty cross-section of column). The figure plots the dimensionless effluent gas concentrations $[y(t)/y^0]$ as functions of dimensionless times (t/t^0) , where t^0 is the stoichiometric breakthrough time for local equilibrium case (Sircar and Kumar, 1983). It shows that the breakthrough curve is almost a step function at dimensionless time of unity which indicates that the kinetics of chemisorption of CO_2 on the material is very fast at 400°C .

Figure 8 shows an example of the CO_2 desorption profile from the chemisorbent (saturated with 65.7% CO_2 + 34.3% N_2 at ambient pressure) by purge with N_2 at 400°C . The N_2 inlet gas mass-flow rate was $3.0 \times 10^{-5} \text{ gmol/cm}^2/\text{s}$. It plots the fraction of CO_2 desorbed $[F = N_{\text{CO}_2}(t)/N_{\text{CO}_2}^0]$ as a function of total effluent gas quantity $[N(t) = \int_0^t Q(t) \cdot dt]$ at any time t . The quantity $N_{\text{CO}_2}(t) = \int_0^t Q(t) \cdot y(t) dt$ is the amount of CO_2 desorbed from the column at time t . $N_{\text{CO}_2}^0$ is the total amount of CO_2 in the column at the start of the desorption test. These quantities were calculated from the experimental desorption effluent gas profiles. The CO_2 desorption characteristics exhibited by Figure 8 are typical for an adsorbate with reversible Type I adsorption isotherm (Sircar and Golden, 1995). We used the isothermal, local equilibrium model for desorption of a Langmuirian sorbate by purge (Sircar and Golden, 1995; Sircar and Kumar, 1985) to describe the data of Figure 8 using the isotherm of Figure 6. The solid line in Figure 8 shows the results. The excellent fit

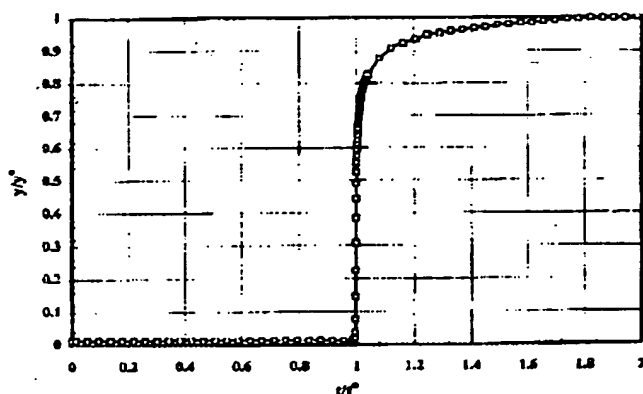


Figure 7. Column breakthrough characteristics for CO_2 on chemisorbent at 400°C using a feed gas containing 65.7% CO_2 and 34.3% N_2 at ambient pressure.

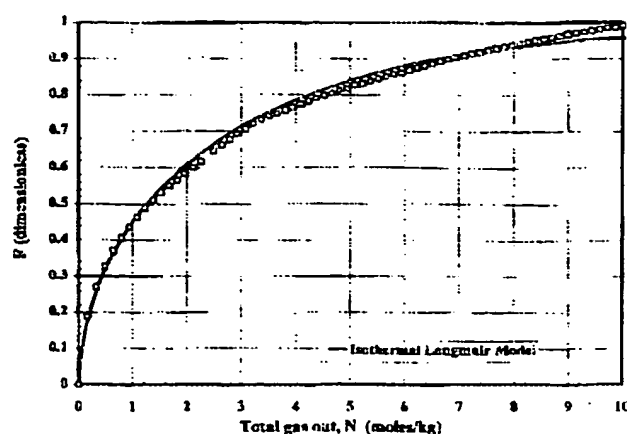


Figure 8. CO_2 desorption characteristics by N_2 purge for chemisorbent saturated with 65.7% CO_2 and 34.3% N_2 at ambient pressure and 400°C .

of the desorption data by the model indicates that CO_2 desorption by purge from the material is essentially local-equilibrium controlled.

The above results indicate that the proprietary material exhibits all of the desirable properties (reversible and substantial CO_2 sorption capacity in presence of steam, fast kinetics, desorption of CO_2 by pressure reduction and purge with a nonadsorbing gas) required for use by the SERP concept.

SERP for Hydrogen Production

The cyclic steps of the Sorption Enhanced Reaction Process for production of H_2 by SMR are as follows (Carvill et al., 1996):

(a) *Sorption-Reaction Step:* Flow mixture of steam and methane at a reaction temperature (T_R) and pressure (P_R) through a tubular catalytic reactor packed with an admixture of a CO_2 chemisorbent and a SMR catalyst. A hydrogen enriched effluent gas containing primarily H_2 and CH_4 at pressure P_R is produced. A part of this effluent gas is withdrawn as the H_2 enriched product gas. The step is continued until the carbon oxide and methane concentrations of the effluent gas reach a preset level (say $\sim 50 \text{ ppm}$ and 5% , respectively).

(b) *Depressurization Step:* The reactor-adsorber is depressurized in a direction countercurrent to that of the feed gas flow from pressure P_R to a pressure of P_D . A gas mixture containing H_2O , H_2 , CO_2 , CO and CH_4 (primarily interparticle-void gas and some desorbed CO_2) is produced. The pressure P_D can be atmospheric or subatmospheric.

(c) *Purge I Step:* The reactor-adsorber is then purged in a direction countercurrent to that of the feed gas flow at pressure P_D with a relatively nonadsorbing gas (such as CH_4 or steam). The effluent gas contains the major part of the desorbed CO_2 from the chemisorbent.

(d) *Purge II Step:* The reactor-adsorber is purged in a countercurrent direction with a part of the H_2 enriched effluent gas produced during step a. The purge effluent gas primarily contains a mixture of H_2O , CH_4 , CO_2 and H_2 .

(e) *Pressurization Step:* The reactor adsorber is then repressurized from P_D to P_R countercurrently with a part of

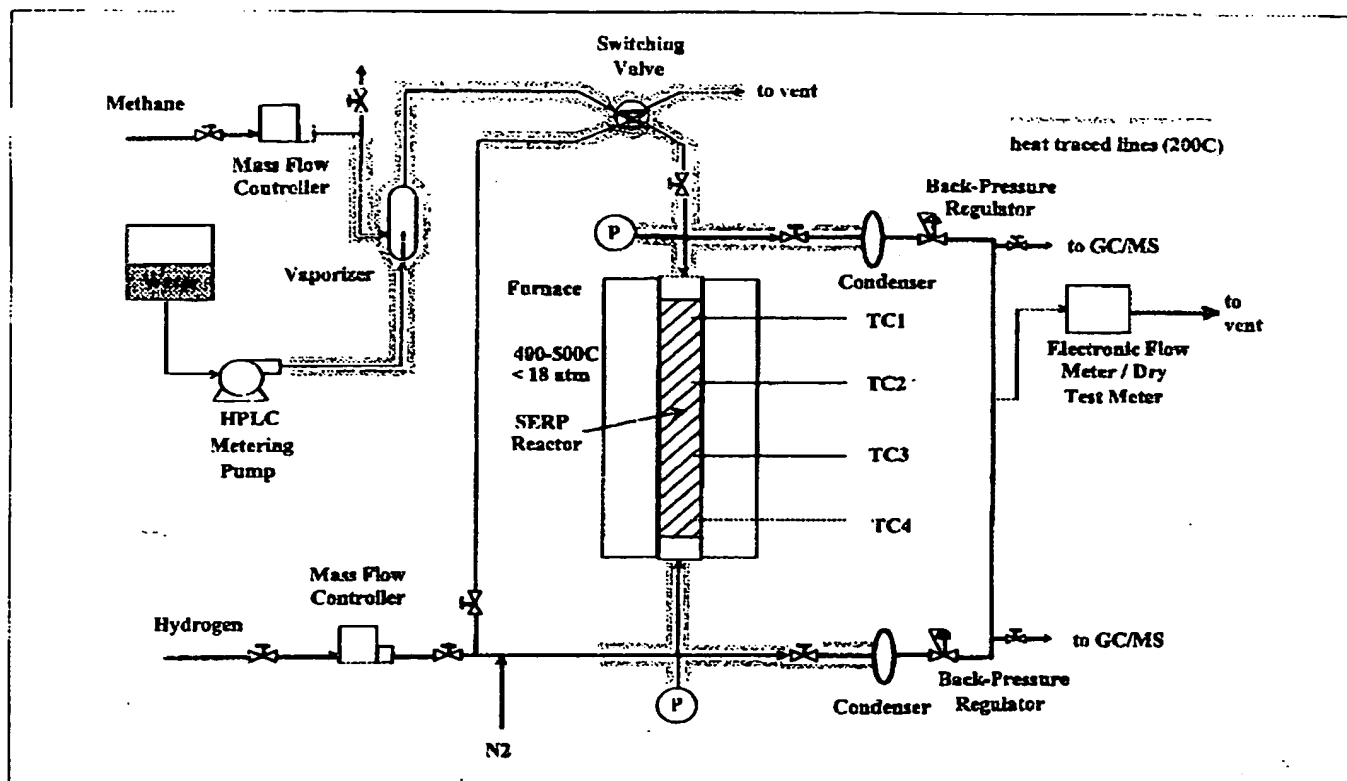


Figure 9. Bench-scale apparatus for testing SERP concept for H_2 production.

the H_2 enriched product gas from step a. The cycle then restarts from step a.

At least two parallel adsorber-reactors are needed by SERP to sustain continuous feed and product gas flows. The cycle times for the steps of the process are such that when one reactor carries out step a, the other reactor goes through steps b-c. The reactors are maintained near isothermal conditions at T_R by indirectly supplying heat of reaction and desorption through the reactor walls.

Bench-Scale Testing of SERP for H_2 Production

The single reactor, bench-scale apparatus described in our previous article (Carvill et al., 1996) was retrofitted to operate SERP for H_2 production. Figure 9 shows the modified apparatus. The stainless steel reactor (internal diameter = 3.8 cm; length = 106.7 cm) was packed with the admixture of proprietary CO_2 chemisorbent and a commercial SMR catalyst (1:1 weight ratio). The total amount of sorbent + catalyst in the reactor was 1.86 kg. The particle diameters of both the sorbent and the catalyst were ~ 0.3 cm. Liquid water was vaporized and mixed with CH_4 to form the SMR feed gas. N_2 at ambient pressure was used as the purge gas for step c. The reactor temperature was maintained at $450 \pm 10^\circ C$ during the steps of the process. The analytical instruments used in the apparatus are described in Figure 9 and elsewhere (Carvill et al., 1996).

The apparatus was designed to evaluate the performance of the individual steps of the SERP in a sequential manner. It was not run continuously.

SERP Column Test Data

An experiment was carried out according to the previously described SERP concept using the apparatus of Figure 9. The feed gas contained a steam:methane mixture in the ratio of 6:1 at a pressure of 55 psig (480.3 kPa) (P_R) and at a temperature of $450^\circ C$ (T_R). The feed gas-flow rate was 3.0×10^{-5} g mol/cm²/s. The purge gas pressure was ~ 2 psig (~ 115.1 kPa) (P_D). The reactor was initially pressurized with H_2 at 55 psig (480.3 kPa) and $450^\circ C$. The quantity of H_2 needed for pressurization was 0.11 mol/kg of total material (sorbent + catalyst) in the column.

Figure 10 shows the effluent gas characteristics for step (a) of SERP for H_2 production. It plots the average cumulative effluent gas H_2 concentration (mol%) on a dry basis as a function of net H_2 product gas quantity (H , mol/kg of total material in column). The plot also shows the average cumulative concentration of CH_4 in the product H_2 . The average concentrations of CO and CO_2 in the product gas are less than 50 ppm. The quantity H is defined as the total amount of product H_2 minus the amount of H_2 used for pressurizing the reactor.

It may be seen from Figure 10 that the sorption-reaction step of the SERP concept at $450^\circ C$ directly produces a substantial quantity of high purity H_2 product (≥ 95 mol%) with methane as the bulk impurity (< 5 mol%) and trace quantities of carbon oxides impurities (< 50 ppm). Obviously, the larger the purity of H_2 in the product gas, the lower will be the H_2 product quantity. The conversion of CH_4 to H_2 for any given value of H can be calculated by knowing the corre-

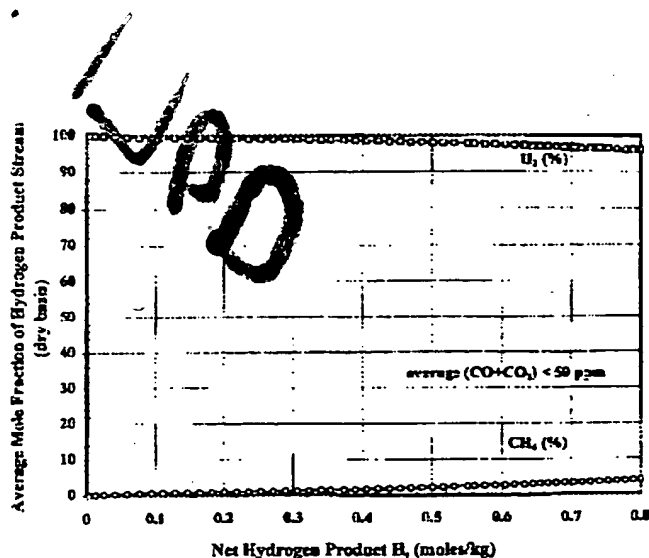


Figure 10. Characteristics of H_2 -enriched product effluent gas produced during sorption-reaction step of SERP concept.

sponding amount of feed CH_4 introduced into the reactor. The conversion is 82% when the net H_2 product is 0.8 mol/kg and the H_2 product purity is 96% (balance CH_4 + trace amounts of CO and CO_2).

Table 1 summarizes the performance of SERP concept for the experiment reported in this work and compares it with the performance of a conventional SMR reactor (without sorbent) for H_2 production at 450°C. The same $H_2O:CH_4$ ratio of the reactor feed gas and reaction pressure (P_R) were used for calculating the performance of the conventional SMR reactor. It may be seen that the SERP concept at 450°C permits production of a much higher purity H_2 product at a much larger CH_4 to H_2 conversion than the catalyst alone case at the same temperature. In particular, the H_2 product gas from the SERP concept is essentially a mixture of H_2 (> 95 mol%) and CH_4 with trace amounts (ppm) of carbon oxides. The conventional SMR process at 450°C, on the other hand, produces an H_2 product containing a much lower concentration of H_2 (53 mol%) and a large quantity (13 mol%) of carbon oxide impurities. Thus, the subsequent purification of H_2 by a PSA system is much easier and simpler for the SERP case.

Table 1 also shows that a reaction temperature of ~ 650°C is required by the catalyst alone case for matching the CH_4 to H_2 conversion of the present SERP case. The H_2 product gas from the corresponding SMR reactor again contains a

moderate concentration of H_2 (75.5 mol%) with a very large amount (20 mol%) of carbon oxide impurities.

The above results demonstrate that the proposed SERP concept can be used to directly produce a purer H_2 stream with trace amounts of carbon oxide impurities at reaction pressure with high conversion of CH_4 to H_2 , while requiring a much lower reaction temperature than the conventional SMR process. The absence of bulk carbon oxide impurities in the H_2 product stream by the SERP concept simplifies the subsequent H_2 purification step by PSA compared to that required for the case of conventional SMR route for H_2 production. For some refinery applications which do not require very high purity H_2 gas, the subsequent H_2 purification step can be completely eliminated by using the SERP concept for H_2 production.

Summary

A Sorption-Enhanced Reaction Process (SERP) concept is described that can be used to directly produce high purity (> 95 mol%) H_2 product containing CH_4 as the bulk impurity (< 5 mol%) and carbon oxides as trace impurities (~ 50 ppm) at the reaction pressure by steam methane reformation. The process allows high conversion of CH_4 to H_2 while operating at a much lower reaction temperature than that required by the conventional equilibrium controlled, endothermic SMR reactor. Thus, the SERP concept offers high potential for cost saving compared to the conventional catalytic SMR route of H_2 production by removing the need for high-temperature reactor metallurgy and by reducing or eliminating the need for subsequent H_2 product purification systems.

The SERP concept uses an admixture of a chemisorbent and a SMR catalyst in the reactor. The chemisorbent selectively removes the undesired reaction product (CO_2) of the SMR reaction from the reaction zone and thus enhances the conversion of CH_4 to H_2 according to Le Chatelier's principle. It also decreases the CO concentration of the product gas. The chemisorbent is periodically regenerated by the principles of pressure swing adsorption (PSA). The steps of the cyclic SERP process are so designed that only a single unit operation is needed to carry out the reaction and the majority of the desired product purification.

A proprietary chemisorbent based on potassium carbonate promoted hydrotalcite is developed for use in the SERP for H_2 production. The material reversibly chemisorbs CO_2 at a temperature of 300–500°C in the presence of excess steam. The chemisorption isotherm of CO_2 on the material is Type I by Brunauer classification. The material provides a substan-

Table 1. Hydrogen Production by SERP and Conventional SMR Process

	Product Purity on Dry Basis (mol%)	CH_4 Conversion (%)	H_2 Productivity (mol/kg)
SERP at 450°C and 55 psig $H_2O:CH_4 = 6:1$	96% H_2 + 4% CH_4 + < 50 ppm (CO + CO_2)	82	0.80
SMR at 450°C and 55 psig $H_2O:CH_4 = 6:1$	53% H_2 + 34% CH_4 + 13% (CO + CO_2)	28	—
SMR at 645°C and 55 psig $H_2O:CH_4 = 6:1$	75.5% H_2 + 4.4% CH_4 + 20.1% (CO + CO_2)	82	—

SI conversion: kPa = (psig + 14.7) × 6.89.

nal CO_2 sorption capacity and it can be regenerated by lowering the superincumbent partial pressure of CO_2 over the sorbent. The kinetics of CO_2 chemisorption and its desorption from the material is fast.

The SERP concept for H_2 production by SMR is experimentally demonstrated using an admixture of the proprietary CO_2 chemisorbent and a commercial SMR catalyst at a temperature of 450°C and a pressure of 55 psig (80.3 kPa). The reactor directly produced a 95+ mol% pure H_2 stream containing 5 mol% CH_4 and less than 50 ppm of carbon oxide impurities using a feed gas containing steam and methane in the ratio of 6:1. The CH_4 to H_2 conversion was 82%. A conventional SMR reactor operated at 450°C (under equivalent feed gas conditions) would produce a H_2 product stream containing 53% H_2 , 34% CH_4 , and 13% carbon oxides with a CH_4 to H_2 conversion of only 28%. A temperature of $\sim 650^\circ\text{C}$ would be necessary for a conventional SMR reactor in order to match the CH_4 to H_2 conversion of the SERP concept operated at 450°C using the same feed gas conditions. The SMR reactor effluent in this case would consist of 5.5% H_2 , 4.4% CH_4 , and 20.1% carbon oxides.

Acknowledgments

The authors are grateful to J. R. Hozowski and J. F. Zenon for carrying out some of the experimental work on preparation of the chemisorbent and generating SERP performance data, respectively. The work was partially supported by the U.S. Department of Energy under cooperative agreement DE-FC 36-95G010059. A portion of this article was presented at the 1998 AIChE Meeting in Miami Beach, FL.

Notation

CO_2 sorbed from chemisorbent by N_2 purge
 product produced during the sorption

y_i = mol % i in effluent gas
 y_i^0 = mol % i in feed gas

y_i = gas phase mole fraction of component i
 y_i^0 = feed gas mole fraction of component i
 χ = mol of H_2 formed per mole of CH_4 introduced in the batch SMR reactor

Literature Cited

- Anand, M., J. R. Hufton, S. Mayorga, S. Nataraj, S. Sircar, and T. R. Gaffney, "Sorption-Enhanced Reaction Process for Production of Hydrogen," *Proc. U.S. DOE Hydrogen Program Rev.*, **1**, 537 (1996).
- Carvill, B. T., J. R. Hufton, M. Anand, and S. Sircar, "Sorption-Enhanced Reaction Process," *AIChE J.*, **42**, 2765 (1996).
- Fudrer, A., and E. Rudekstorfer, "Selective Adsorption Process," U.S. Patent 3,986,849 (1976).
- Hayward, D. O., and B. M. W. Trapnell, *Chemisorption*, Butterworths, Washington, p. 159 (1964).
- Hufton, J. R., S. Mayorga, T. R. Gaffney, S. Nataraj, M. B. Rao, and S. Sircar, "Sorption-Enhanced Reaction Process for Production of Hydrogen," *Proc. U.S. DOE Hydrogen Program Rev.*, **2**, 623 (1998).
- Leiby, S. M., "Options for Refinery Hydrogen," PEP Report No. 212, Process Economics Program, SRI International, Menlo Park, CA (Feb., 1994).
- Sircar, S., and T. C. Golden, "Isothermal and Isobaric Desorption of Carbon Dioxide by Purge," *I&EC Res.*, **34**, 2881 (1995).
- Sircar, S., and W. C. Kratz, "Simultaneous Production of Hydrogen and Carbon Dioxide from SMR Off-gas by Pressure Swing Adsorption," *Sep. Sci. Tech.*, **23**, 1397 (1988).
- Sircar, S., M. Anand, B. T. Carvill, J. R. Hufton, S. Mayorga, and R. N. Miller, "Sorption Enhanced Reaction Process for Production of Hydrogen," *Proc. U.S. DOE Hydrogen Program Rev.*, **1**, 815 (1995).
- Sircar, S., and R. Kumar, "Equilibrium Theory for Adiabatic Desorption of Bulk Binary Gas Mixtures by Purge," *I&EC Proc. Des. and Dev.*, **24**, 358 (1985).
- Sircar, S., and R. Kumar, "Adiabatic Adsorption of Bulk Binary Gas Mixture: Analysis by Constant Pattern Model," *I&EC Proc. Des. & Dev.*, **22**, 271 (1983).
- Twigg, M. V., ed., *Catalyst Handbook*, Wolfe, London (1989).
- Wagner, J. L., "Selective Adsorption of Gases," U.S. Patent 3,430,418 (1969).
- Young, D. M., and A. D. Crowell, *Physical Adsorption of Gases*, Chap. I, Butterworths, Washington (1962).

Manuscript received Oct. 6, 1998, and revision received Dec. 21, 1998.

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